Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Polymer 46 (2005) 4991–5000

polymer

www.elsevier.com/locate/polymer

Anionic polymerization of acrylates. XIV. Synthesis of MMA/acrylate block copolymers initiated with ester-enolate/*tert*-alkoxide complex

Petr Vlček*, Eva Čadová, Jaroslav Kříž, Petra Látalová, Miroslav Janata,
Luděk Toman, Bohumil Masař

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

Received 16 February 2005; received in revised form 15 April 2005; accepted 26 April 2005

Abstract

Diblock copolymers of methyl methacrylate (MMA) with 2-ethylhexyl, butyl, ethyl or *tert*-butyl acrylate (EtHA, BuA, EtA, *t*-BuA) have been prepared by the ligated anionic polymerization initiated with methyl 2-lithioisobutyrate (MIB-Li) in the presence of an excess of Li *tert*-butoxide (*t*-BuOLi) in toluene/THF mixture at −60 or −78 °C. The copolymers, prepared at −60 °C, show MWD with a hint of bimodality, indicating partial deactivation of the living PMMA upon addition of acrylic monomer. At −78 °C, the extent of this deactivation is distinctly lower, the formed block copolymers, in particular, poly(MMA-*b*-EtHA), have unimodal MWD and exhibit tails only in the lower-molecular-weight region. Poly(MMA-*b*-EtHA)s were extracted with acetonitrile dissolving PMMA; very small parts of the crude products dissolved, whereas prevailing parts remained as solids documenting thus formation of block copolymer in a high yield. Surprisingly, the highest amount of self terminated PMMA was found in block copolymerization of MMA with *t*-BuA at both the temperatures, the products of which had clearly bimodal MWDs. This finding is shortly discussed on the basis of relatively slow propagation of *t*-BuA in comparison with EtHA, BuA and EtA.

Keywords: Ligated anionic polymerization; (Meth)acrylates; Block copolymers

1. Introduction

Anionic polymerization of acrylic and methacrylic esters is accompanied by a number of undesired reactions causing lack of control over the process [1–4]. Various initiating systems have been developed to overcome these complications [5–8]. One of the successful methods is the ligated anionic polymerization (LAP) using complex initiators, composed of a true initiating compound and various stabilizing ligands, restricting the extent of side reactions [9,10]. First, alkali metal *tert*-alkoxides were used for this purpose [10–12]. Later on, the spectrum of utilizable ligands was extended by LiCl [13,14], bidentate lithium alkoxides (e.g. Li 2-(2-methoxyethoxy)ethoxide, MEEOLi) [15–17], alkylaluminiums [18–21], Li perchlorate [22], Li silanolates [23], etc. Such ligands form with the initiator used and/or with growing chain-ends cross-complexes of various compositions, modifying thus the immediate environment of the living macroanion. Consequently, these complexes lower the reactivity of the negatively charged chain-end in undesired condensation reactions with the carbonyl of the monomer and/or polymer. The complexes have been studied in model systems, using esters of carboxylic acids metalated in position 2 as low-molecular-weight models of living methacrylate growing chain-ends [24–26]. The structure and composition of the complexes depend on the type and mole ratio of the components, temperature and storage time. In the case of *tert*-alkoxides, formation of cross-aggregates is a stepwise process [25,27]. When methyl 2-lithioisobutyrate (MIB-Li) is mixed with Li *tert*-butoxide (*t*-BuOLi) in THF solution, the alkoxide gradually replaces metaloester molecules in the MIB-Li tetramer. At room temperature, the complex with the MIB-Li/*t*-BuOLi mole ratio 1:1 is formed first, which is further transformed to the 2:2 complex and, finally, after sufficiently long storage, the 1:3 complex is obtained (Scheme 1). This equilibrium mixture contains all

---

* Corresponding author. Tel.: +420 296 809 250; fax: +420 296 809 410.

E-mail address: vlcek@imc.cas.cz (P. Vlček).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.04.059

$$3\,[(\text{MIB-Li})_4] + (t\text{-BuOLi})_4 \longrightarrow 4\,[(\text{MIB-Li})_3(t\text{-BuOLi})_1]$$

$$2\,[(\text{MIB-Li})_3\,(t\text{-BuOLi})_1] + (t\text{-BuOLi})_4 \rightleftharpoons 3\,[(\text{MIB-Li})_2\,(t\text{-BuOLi})_2]$$

$$[(\text{MIB-Li})_2\,(t\text{-BuOLi})_2] + (t\text{-BuOLi})_4 \rightleftharpoons 2\,[(\text{MIB-Li})_1\,(t\text{-BuOLi})_3]$$

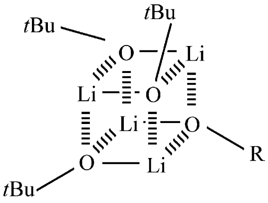
Scheme 1.

three abovementioned cross-complexes with the 1:3 complex slightly prevailing.

The equilibrium is reached after storing the mixture with three-fold excess of *t*-BuOLi over the MIB-Li at −15 °C for 24 h or within approximately 5 min at room temperature if the excess of the alkoxide over the initiator is 6 or more. The core of the cross-aggregates has a cubic structure, in which C and O atoms alternate (Scheme 2).

The equilibrium mixtures of MIB-Li with *t*-BuOLi are advantageous initiators of controlled anionic polymerization of methacrylate esters affording active centers with high stability so that three consecutive MMA doses can be successfully polymerized giving the final product with unimodal and narrow MWD [28,29]. In our recent work [30], synthesis of di- and tri-block methacrylate copolymers was described, proceeding in a living manner without a detectable extent of side reactions, in particular the spontaneous termination of growing chain-ends by backbiting reaction. However, block copolymerization MMA/*tert*-butyl acrylate (*t*-BuA) indicated that some self-termination occurs during an early stage of *t*-BuA polymerization initiated with the living PMMA macroinitiator. This feature was already mentioned by other authors in a study of MMA/*t*-BuA block and random copolymerizations initiated with the systems containing LiCl ligand [31,32].

Block copolymers composed of hard PMMA and rubbery polyacrylate blocks (PEtHA, PBuA, PEtA) can find use in a number of applications such as thermoplastic elastomers or compatibilizers of polymer blends composed of PMMA resin and acrylate rubbers. However, due to a high reactivity and, in particular, due to a high tendency of acrylic esters to side reactions, controlled anionic polymerization of acrylates requires specific approach and conditions to reach a ‘living’ process. This is why various research groups have been developing appropriate initiating systems guaranteeing that the polymerization is sufficiently ‘living’ for tailoring polyacrylates and, in particular, block copolymers with acrylate blocks. Good results were obtained when polymerizing MMA first with a metalloporphyrin initiator in CH_2Cl_2 and using the living PMMA as macroinitiator for *t*-BuA, EtA and isobutyl acrylate [33]. Also, lanthanocene-type initiators give well-controlled polymerization of acrylate and methacrylate esters [8,34] and can be used for preparation of block copolymers. For instance, living polymethacrylate can be prepared at 0 °C and subsequently used for initiation of BuA polymerization giving poly(MMA-*b*-BuA) with good molecular parameters. Moreover, random copolymerization of MMA/acrylate mixtures leads also to products with an almost block character because the acrylate reactivity differs in several orders of magnitude from that of methacrylates [35].



Scheme 2.

As to LAP, acrylic esters require ligands with a high stabilizing efficiency so that, for instance, LiCl or Li silanolates ensure neither controlled polymerization of acrylates (excepting *t*-BuA) nor their block copolymerization with MMA. The best results were obtained in a polymerization initiated with (diphenylmethyl)lithium (DPMLi) in the presence of ten-fold excess of MEEOLi at −78 °C in toluene/THF 9/1 or 75/25 (v/v) mixtures [36,37]. Di- and tri-block copolymers of MMA with EtHA, BuA and nonyl acrylate were successfully prepared in this way, having expected molecular parameters and narrow MWDs, with no appreciable content of homopolymer from the first polymerization step. However, MMA has to be polymerized as the first and the acrylate as the second monomer; for the opposite monomer order, products have bimodal MWDs and are always contaminated with polyacrylate homopolymers. Similarly, poly(*t*-BuA-*b*-EtHA) and poly(*t*-BuA-*b*-BuA) were synthesized using *tert*-butyl 2-lithioisobutyrate (tBIB-Li) initiator in the presence of a *t*-BuOLi excess in a toluene/THF mixture [38]. In the present study, the equilibrium complex MIB-Li/*t*-BuOLi has been used for controlled preparation of copolymers of MMA with EtHA, BuA, EtA and *t*-BuA.

2. Experimental

2.1. Materials

MMA, EtHA, BuA, *t*-BuA and EtA monomers (Fluka) were distilled first with CaH_2 and, prior to use, purified by vacuum distillation with triisobutylaluminium. THF and toluene (Fluka) were first distilled with CaH_2 and then, just before use, with sodium benzophenone complex. Synthesis and purification of MIB-Li and *t*-BuOLi were described earlier [39,40]. Methanol and acetonitrile (Fluka) were used as received.

2.2. Synthesis of copolymers

Block copolymerizations were performed at chosen temperature (−60 or −78 °C) in a tank reactor equipped with an external stirrer, argon inlet, side dosing cells and stainless capillary with gas-tight stopcock for sample withdrawal [41]. All manipulations were performed in dry argon, conversions of monomers were determined gravimetrically or by gas chromatography (GC). Typically, synthesis of poly(MMA-*b*-EtHA) diblock was run as follows: The reactor was dried by heating with flame under vacuum and flushing with argon; the cycle was repeated 10 times. After that, 38 ml of dry toluene and 20 ml of dry THF containing 0.75 mmol of MIB-Li and 7.5 mmol of *t*-BuOLi were introduced into the main vessel of the reactor and the device was put into a −60 °C bath. One of the dosing cells was filled with 18 ml of dry toluene and 4 ml (37.4 mmol) of MMA and left to cool down to the reaction temperature (ca. 5 min). Then, the monomer solution was quickly transferred into the main vessel under vigorous stirring using argon overpressure and polymerized at a given temperature for 1.5 h. After this time interval, a 30 ml sample of reaction mixture was withdrawn for SEC analysis, using argon overpressure and the stainless capillary mentioned above. Then, 25 ml of toluene and 4.9 ml (23.4 mmol) of EtHA were introduced into the second dosing cell, left to cool down to the reaction temperature, transferred into the main reactor vessel and polymerized for 20 min. The reaction was terminated by adding a methanol/THF mixture. Conversions of MMA in the first step and EtHA in the second step were over 95%, as determined by GC. The product was isolated and purified by precipitation into a 9/1 (v/v) methanol/water mixture.

2.3. Analyses of polymers

Molecular weights and polydispersities of products were determined by SEC, using a Labora HP-5001 apparatus (Czech Republic) in THF at 20 °C with a separation system composed of two 300×8 mm columns (PSS Germany) filled with SDV gel (bead size 5 μm, porosity 10^5 and 10^3 Å), equipped with differential refractometer Labora RIDK 102 and UV detector Labora LCD 2040 ($\lambda = 260$ nm). The flow rate of THF was 1 ml/min, the system with separation range 10^3–10^6 Da was calibrated with PMMA standards (PSS Germany). Eluograms were mostly treated as PMMA [42] using Caliber software (Polymer Laboratories). As the molecular weights of block copolymers, obtained from SEC are only apparent values, more accurate data were calculated from composition of copolymers, determined by ^{1}H NMR.

2.4. NMR measurements

^{1}H NMR spectra of 5% wt solutions of polymers in $CDCl_3$ with HMDS as internal standard were measured at 300.13 MHz using a Bruker Avance DPX 300 spectrometer. The measurements were performed at 330 K under the following conditions: pulse width 15.3 μs (90° pulse), relaxation delay 10 s, spectral width 6000 Hz, acquisition time 1.36 s, 16 scans. The intensities were calculated using integrating software of the spectrometer. Compositions of copolymers were determined from the integrated relative intensities of the peaks at 3.58 ppm (OCH_3 in MMA) and 3.9–4.1 ppm (OCH_2– in EtHA, BuA and EtA).

2.5. Extraction tests

Final products of block copolymerization of MMA and EtHA, prepared at different temperatures, were extracted with acetonitrile (AN) to separate self-terminated PMMA formed in the first polymerization step and the corresponding poly(MMA-*b*-EtHA) copolymer. AN is a good solvent for PMMA and does not dissolve PEtHA. A known amount of crude copolymerization product was introduced into a flask, AN was added and the mixture was vigorously shaken at room temperature for 18 h. Then, the insoluble fraction was separated by centrifugation, the solution carefully transferred by syringe into a weighed flask and AN was evaporated. Both the AN-soluble and insoluble fractions were dried in vacuo at 40 °C, weighed and analyzed by SEC and NMR.

3. Results and discussion

3.1. Block copolymerization of MMA and EtHA

To prepare poly(MMA-*b*-EtHA) diblock copolymers, MMA was polymerized in the first step at chosen temperature in a 50/50 (v/v) toluene/THF mixture, initiated with the MIB-Li/*t*-BuOLi complex. The MMA/MIB-Li/*t*-BuOLi mole ratio was 50/1/10 or 100/1/10, see Table 1. After completion of MMA polymerization, a sample of the reaction mixture was withdrawn for analysis and, subsequently, a toluene solution of EtHA, precooled to the reaction temperature, was added (Section 2). Thus, the toluene/THF volume ratio was approximately 65/35 in the second polymerization step. The mixed solvent was chosen with respect to the results of EtHA polymerization initiated either with tBIB-Li in the presence of *t*-BuOLi [12] or with alkyllithium-type initiators combined with MEEOLi [37] as stabilizing ligand. Reaction times of the experiment performed at −60 °C (run 1) were 90 min for the first and 20 min for the second step and conversions of both the monomers were ca. 95%. Let us note that the polymerization of the acrylate initiated with living PMMA macroinitiator proceeds rapidly and, thus, EtHA is almost quantitatively consumed within a couple of minutes. As can be seen from Table 1, molecular weight of the final product is distinctly higher than that of the corresponding PMMA precursor and the polydispersity index ($M_w/M_n = 1.20$), calculated from the total eluogram (Fig. 1, trace 2), is slightly higher than that of the PMMA homopolymer ($M_w/M_n = 1.16$). Nevertheless, the eluogram shows bimodal MWD of the copolymerization product containing a low-molecular-weight part having a retention time comparable with that of the PMMA precursor. This indicates that a part

Table 1

Run	T (°C)	1st step[a]			2nd step			
		MMA (mmol)	SEC		EtHA (mmol)	SEC		M_n (theor)[b]
			M_n	M_w/M_n		M_n	M_w/M_n	
1	−60	23.4	6700	1.16	23.5	22,000[c], 31,700[d]	1.20 1.04	19,400
2	−78	13.1	7700	1.23	13.0	21,800[c]	1.12	22,100
3[e]	−78	23.4	20,200	1.08	47.1	88,000[c,f], 108,000[d,f]	1.26 1.11	94,200

[a] MMA:MIB-Li:*t*-BuOLi mole ratio = 50:1:10; toluene/THF 50/50 (v/v).

[b] Theoretical M_n values of copolymers calculated from concentrations of living PMMA from the first step and amounts of EtHA consumed in the second step.

[c] Calculated from total eluogram, i.e. major peak plus low-molecular-weight peak or tail.

[d] Calculated from the major peak only.

[e] MMA:MIB-Li:*t*-BuOLi mole ratio = 100:1:10.

[f] Calculated as PEtHA.

of the living PMMA macroinitiator does not form a real block copolymer but self terminates just after addition of a few acrylate monomer units. The idea is corroborated by a UV absorption of the low-molecular-weight part at $\lambda = 260$ nm (trace 3) caused most probably by the presence of a conjugated system of C=C and C=O double bonds in the polymer. As suggested earlier [32,43], such structural motif most probably corresponds to the enol form of a cyclic ketoester, formed by a back-biting reaction either in a purely polyacrylate living chain or a polymethacrylate with one or two acrylate units attached at its end.

Distinctly better results were obtained in run 2, polymerized at −78 °C. Here, MMA was polymerized for 180 min, then a sample of PMMA was withdrawn for analyses, a precooled toluene solution of EtHA was added and polymerized for 30 min. The refractometric trace of the SEC eluogram (Fig. 2, trace 2) of the final product exhibits an almost negligible tail towards the low-molecular-weight region without any indication of bimodality. As this tail absorbs in UV region at 260 nm (trace 3), it can be assumed that it consists of PMMA chains with short PEtHA blocks having cyclic ketoester groups at the ends. MWD of the final product, calculated from the eluogram including the tail, is narrow, even narrower than that of the PMMA from the first reaction step ($M_w/M_n = 1.12$ and 1.23, respectively; see Table 1).

The final product of the block copolymerization performed at −78 °C is thus virtually a pure poly(MMA-*b*-EtHA) copolymer, containing no perceptible amount of the PMMA homopolymer.

Run 3 in Table 1 is an attempt to prepare poly(MMA-*b*-EtHA) diblock with both the blocks longer than in the foregoing experiments. In the first step, the MMA:MIB-Li:*t*-BuOLi mole ratio was 100:1:10 and MMA was polymerized at −60 °C for 2 h; then, the temperature was lowered to −78 °C and the mixture was stored for additional 90 min. After that, a sample of the living PMMA was withdrawn for analysis, toluene solution of EtHA was added and polymerized at the same temperature for 30 min. The MMA/EtHA mole ratio was ca. 1:2 in this case and the product should contain PEtHA block twice longer than the PMMA one. Both the monomers were consumed quantitatively and the final product has a narrow MWD with somewhat non-symmetric SEC eluogram, exhibiting a

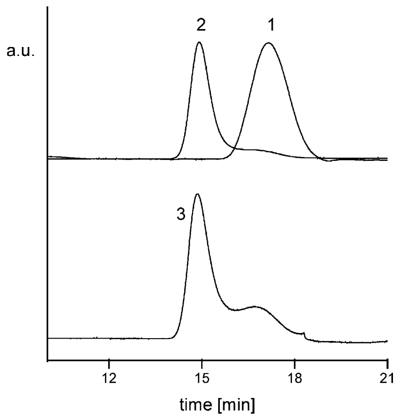


Fig. 1. MMA/EtHA block copolymerization (run 1, Table 1), SEC eluograms of the products: (1) PMMA homopolymer, RI detection, (2) final product, RI detection and (3) final product, UV detection.

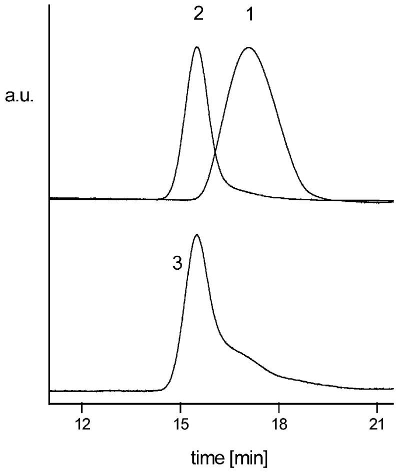


Fig. 2. MMA/EtHA block copolymerization (run 2, Table 1), SEC eluograms of the products: (1) PMMA homopolymer, RI detection, (2) final product, RI detection and (3) final product, UV detection.

tail towards the low-molecular-weight region (Fig. 4, trace 2). Nevertheless, M_n and M_w/M_n calculated from the major peak (Table 1) indicate the formation in a good yield of an expected block copolymer with rather high molecular weight and acceptable MWD. This is documented also by the results of extraction test (see below).

3.1.1. Extraction tests

To get more information about copolymerization products, crude poly(MMA-*b*-EtHA) copolymers were extracted with acetonitrile (AN), which does not dissolve PEtHA but is a good solvent for PMMA.

The copolymer, prepared at −60 °C (Table 1, run 1) was extracted at room temperature and, surprisingly, a low portion of the crude sample dissolved in AN (6% w/w only), whereas the rest (94%) remained as a solid, insoluble portion. Both the soluble and insoluble portions were dried and analyzed by SEC and ^{1}H NMR; for results, see Table 2. By NMR analysis, this 'purified' copolymer (AN-insoluble portion) contains 42 mol% MMA and 58% EtHA units (Table 2), which is not too far from the initial concentration of the monomers, when the MMA/EtHA mole ratio was ca. 50/50; see Table 1. M_n of the insoluble portion, calculated using the M_n value for the PMMA homopolymer and the MMA/EtHA mole ratio obtained from NMR analysis is 23,700, whereas theoretical M_n value of the poly(MMA-*b*-EtHA) should be ca. 19,400 (Table 1), assuming that the living PMMA macroinitiator was quantitatively used for the formation of copolymer.

The AN-soluble portion can probably contain PMMA chains with self-terminated short PEtHA blocks and PMMAs with terminal cyclic ketoesters composed of MMA and EtHA units. According to NMR analysis, the MMA/EtHA mole ratio is 93/7, i.e. the soluble portion contains mainly PMMA (Table 2). Calculated from M_n of the corresponding PMMA homopolymer and the composition of this portion determined by NMR, M_n of the AN-soluble portion is 7700, i.e. near the molecular weight of the PMMA precursor.

Somewhat different results were obtained from extraction of sample 2 (run 2, Table 1), prepared at −78 °C. Again, ca. 6% w/w of the crude sample was soluble in AN, and 94% remained as a solid portion; for results, see Table 2 and Fig. 3. The solid portion exhibits very narrow MWD without any hint of bimodality or tailing even on the SEC trace obtained from UV detector (Table 2 and Fig. 3, traces 3). By NMR, it is composed of 46 mol% of MMA and 54 mol% of EtHA units. Therefore, M_n of this portion, calculated from M_n of the PMMA homopolymer and NMR analysis, is equal to 24,100, which is near the theoretical value 22,100 (Table 1), calculated from the concentration of living PMMA chains and amount of EtHA consumed in the second step. Clearly, the final product of copolymerization at this temperature is virtually a pure poly(MMA-*b*-EtHA) copolymer with symmetric and very narrow MWD and without contamination by the corresponding homopolymer. The AN-soluble portion (traces 4) contains 12% of PEtHA units, i.e. somewhat more than the AN-soluble portion of sample 1 (see above). This could indicate a slightly lower extent of self-termination of living PMMA chains after addition of acrylate at the lower temperature. Let us note that the AN-soluble portions in both cases contain poly(MMA-*b*-EtHA) chains with relatively long PMMA and short PEtHA blocks. Such copolymers are present in the final copolymerization products, regardless of reaction temperature; however, their content is negligible in copolymers prepared at the lower temperature.

When poly(MMA-*b*-EtHA) copolymer with high molecular weight (run 3, Table 1) was extracted with AN, ca. 3% (w/w) only of the crude product dissolved and the rest remained as a solid phase (Table 2). The eluograms of the crude product and both the fractions are given in Fig. 4. Molecular weight of the insoluble fraction, $M_n = 104{,}300$ as determined by SEC, is very close to the $M_n = 108{,}000$, calculated from the main peak of the crude product eluogram (Table 1 and Fig. 4, traces 2). Also, both these M_n values are near the molecular weight of the AN-insoluble portion ($M_n = 109{,}800$), calculated from the molecular weight of the PMMA precursor and NMR

Table 2
Extractions of crude poly(MMA-*b*-EtHA) copolymers with acetonitrile

Fraction	Amount (% w/w)	SEC		NMR		
		M_n	M_w/M_n	MMA (mol%)	EtHA (mol%)	M_n
Crude product 1	100	22,000	1.20	44	56	22,400
AN-soluble	6	8300	1.16	93	7	7700
AN-insoluble	94	32,400	1.05	42	58	23,700
Crude product 2	100	21,800	1.12	48	52	23,000
AN-soluble	6	8500	1.42	88	12	9600
AN-insoluble	94	24,400	1.07	46	54	24,100
Crude product 3	100	88,000[a]	1.26	32	68	99,700
AN-soluble	3	24,100	1.07	–	–	–
AN-insoluble	97	104,300[a]	1.22	29	71	109,800

The numbers with crude products correspond to the run numbers in Table 1.

[a] Calculated as PEtHA.

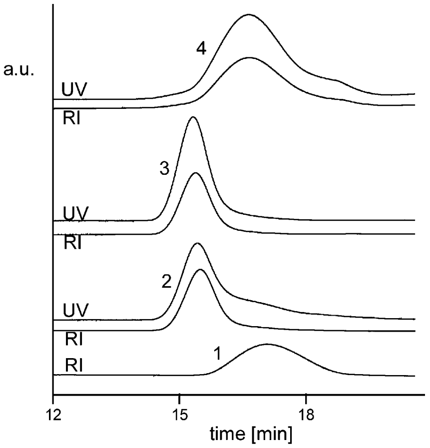


Fig. 3. Extraction of sample 2, Table 1: SEC eluograms of (1) PMMA homopolymer; (2) crude copolymerization product; (3) AN-insoluble portion; (4) AN-soluble portion.

analysis of the copolymer. Eluograms were treated as PEtHA in this experiment, using the corresponding constants of the Mark–Houwink–Sakurada equation [44].

3.2. Block copolymerization of MMA with BuA or EtA

The tendency of acrylic esters to side reactions in anionic polymerization, in particular to self-termination of growing chains by back-biting reaction, increases appreciably with decreasing length and branching of the their alkoxy group. This is why attempts have been made to synthesize block copolymers of MMA with BuA or EtA under the same conditions as in the MMA/EtHA block copolymerizations, discussed in the foregoing paragraph. The results are presented in Table 3.

At −60 °C, MMA was polymerized for 100 min and the added BuA for 25 min; both monomers were consumed virtually quantitatively within these time intervals; see run 1 in Table 3. Molecular weight of the final product is distinctly higher than that of the PMMA homopolymer. However, its MWD is broader and a SEC eluogram of the product (Fig. 5, trace 2) shows an appreciable hint of bimodality, indicating partial self-termination of living PMMA chains after addition of BuA. The position of this shoulder is close to that of the PMMA precursor (Fig. 5, trace 1), i.e. both the molecular weights are also comparable. Due to its strong UV absorption at $\lambda = 260$ nm (trace 3), the chains likely contain PMMA blocks with terminal ‘chemically heterogeneous’ ketoesters formed by MMA and BuA units and poly(MMA-*b*-BuA) copolymers with short PBuA blocks self-terminated with cyclic ketoesters formed exclusively by BuA units. Thus, at the given temperature, a part of the PMMA precursor is most probably deactivated in this way (like in the MMA/EtHA block copolymerization, see above) and does not participate in the generation of a true block copolymer composed of correspondingly long blocks.

Distinctly better results were obtained in block copolymerization performed at −78 °C, (Table 3, run 2) in which MMA was polymerized for 180 min and BuA in the second step for 25 min. In the first polymerization step as well as in the final reaction mixture, only traces of the monomers were found by GC, therefore, conversions of both the monomers are close to quantitative. MWD of the final product is almost the same as that of the PMMA homopolymer ($M_w/M_n = 1.26$ and 1.28, respectively) and its SEC eluogram (Fig. 6, trace 2) exhibits tailing only towards the lower molecular weights, but no hint of bimodality. An attempt to extract the copolymer with AN and separate in this way possibly present unreacted PMMA failed due to the fact that the crude product of copolymerization was completely soluble in this solvent. It can be said that under these reaction conditions and at a low reaction temperature, a copolymer poly(MMA-*b*-BuA) with acceptable molecular parameters was formed in a good yield. Nevertheless, the presence of a certain, probably very low amount of diblock copolymers

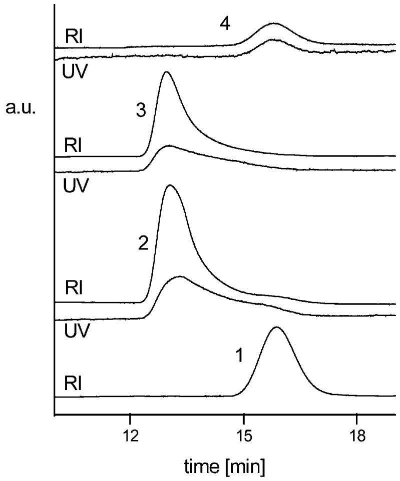


Fig. 4. Extraction of sample 3, Table 1: SEC eluograms of (1) PMMA homopolymer; (2) crude copolymerization product; (3) AN-insoluble portion; (4) AN-soluble portion.

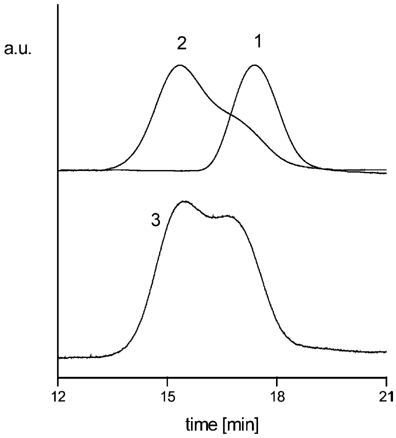


Fig. 5. MMA/BuA block copolymerization (run 1, Table 3), SEC eluograms of the products: (1) PMMA homopolymer, RI detection; (2) final product, RI detection and (3) final product, UV detection.

Table 3
Block copolymerization of MMA with BuA or EtA

Run	T (°C)	1st step[a]			2nd step						
		MMA (mmol)	SEC		Type	M_2 (mmol)	Conv. (%)	SEC		NMR	
			M_n	M_w/M_n				M_n	M_w/M_n	m_1:m_2[b]	M_n
1	−60	34.1	7900	1.17	BuA	36.5	100	18,600	1.48	–	–
2	−78	34.1	6500	1.28	BuA	36.5	100	18,500	1.26	0.92:1	15,600[c]
3	−60	33.9	6200	1.24	EtA	34.1	90	11,900	1.44	–	–
4	−78	36.0	6400	1.34	EtA	34.1	92	13,900	1.36	1.19:1	11,800[d]

[a] MMA:MIB-Li:*t*-BuOLi mole ratio = 50:1:10; toluene/THF 50/50 (v/v).

[b] MMA:acrylate mole ratio in copolymer.

[c] Theoretical $M_n = 15{,}200$ as calculated from the concentration of living PMMA from the first step and the amount of BuA consumed in the second step.

[d] Theoretical $M_n = 12{,}000$ as calculated from the concentration of living PMMA from the first step and the amount of EtA consumed in the second step.

with relatively long PMMA blocks and short PBuA blocks in the product can be reasonably expected. The mole ratio of MMA/BuA units in the copolymer was calculated from ^{1}H NMR spectrum (Fig. 7) and corresponds well to the mole ratio of monomers in copolymerization.

Block copolymerization of MMA and EtA offered similar results as those of MMA and BuA (Table 3, runs 3 and 5). At −60 °C, run 3, polymerization of EtA, initiated with the living PMMA macroinitiator, proceeds up to 90% conversion within 30 min. MWD of the final product is broader than that of PMMA homopolymer; polydispersity indexes M_w/M_n are 1.44 for copolymer and 1.24 for PMMA. Due to an incomplete EtA conversion in the second step, it is clear that under the given conditions, self-termination of the growing PEtA chains is not lowered sufficiently and proceeds to a considerable extent. This finding is in accordance with our previous results on EtA polymerization initiated with tBIB-Li/*t*-BuOLi system under otherwise comparable conditions [45].

When performed at −78 °C (run 4), MMA/EtA block copolymerization gives a product with the M_w/M_n ratio almost the same as that of the corresponding PMMA macroinitiator. However, EtA conversion is again incomplete and SEC eluogram of the final product (Fig. 8, trace 2) is somewhat non-symmetrical. It can be assumed that self-termination of the growing PEtA blocks proceeds to a lesser extent in comparison with the copolymerization at −60 °C; nevertheless, it cannot be fully excluded even at the lower temperature. Regardless of this fact, poly(MMA-*b*-EtA) copolymer with acceptable molecular parameters and only slightly broadened MWD can be prepared in the way presented here. The composition of copolymer is in fair agreement with the amounts of the monomers used, taking into consideration their conversions. Also, the $M_n = 11{,}800$ obtained from SEC measurement and ^{1}H NMR analysis (Table 3) is near to the theoretical value (12,000) calculated from the amount of living PMMA chains and the amount of EtA consumed in the second step.

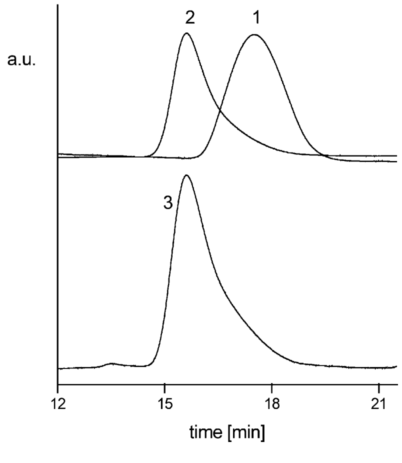


Fig. 6. MMA/BuA block copolymerization (run 2, Table 3), SEC eluograms of the products: (1) PMMA homopolymer, RI detection; (2) final product, RI detection and (3) final product, UV detection.

It follows from the data presented above that results of methacrylate/acrylate block copolymerization depend—among others—on the chemical structure of acrylate. Tendency of acrylic esters to side reactions in anionic polymerization, namely spontaneous termination by back-biting reaction, is determined by the length and branching of the alkoxygroup, distinctly decreasing in the order EtA > BuA > EtHA. This was strongly indicated by the results given in our foregoing papers devoted to ligated anionic polymerization of EtHA, BuA and EtA initiated with the ester enolate/*tert*-alkoxide system. The results clearly document that the rates of self-termination of the esters, expressed as rate constants k_t, increase in the same order, i.e. EtHA < BuA < EtA [45,46,50]. The same tendency was also observed in polymerizations of various acrylates initiated with bulky Li initiators like 1,1-diphenylhexyllithium in the presence of ten-fold excess of MEEOLi. Here, the found polydispersity indexes were ca. 1.05–1.1 for EtHA [51], 1.10–1.30 for BuA [16], 1.30–1.55 for EtA and 1.50–1.60 for methyl acrylate polymerizations in toluene/THF mixture at −78 °C. Also poly(MMA-*b*-BuA) copolymers, prepared with the same system, exhibit slightly broader MWD than poly(MMA-*b*-nonyl acrylate) [37] probably as a consequence of a favorable effect of the longer nonyl group. However, no discussion of the extent of possible self-termination or SEC traces from UV detection was

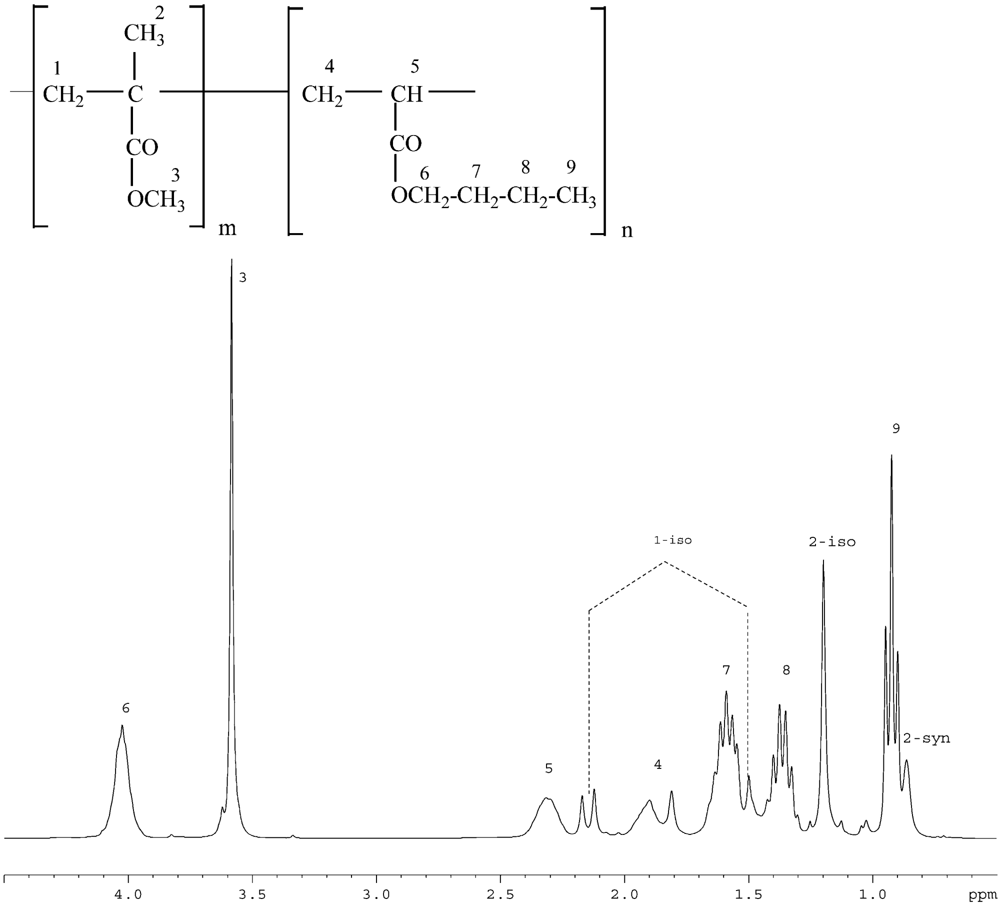


Fig. 7. ^{1}H NMR spectrum of poly(MMA-*b*-BuA), run 2, Table 3.

presented. Thus, the effect of alkoxy group structure seems evident in acrylate polymerizations as well as in their block copolymerizations with MMA. In addition, the *s*-BuLi/Li-silanolate initiating system was used for synthesis of poly(MMA-*b*-BuA)s at low temperature, but the products had bimodal MWDs. An explanation, based on the assumption of multiplicity of active species was presented [52]. Moreover, the order of additions of monomers is of crucial importance due to different stabilities of living methacrylates and acrylates. Generally, methacrylate must be polymerized first. However, an attempt was made to prepare poly(EtHA-*b*-MMA) using MEEOLi additive and the opposite order of addition of the monomers [36]. The pure copolymer was formed at −100 °C only; at −78 °C, a bimodal product was always obtained.

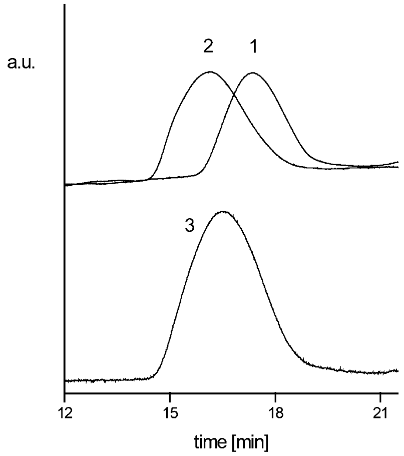


Fig. 8. MMA/EtA block copolymerization, (run 4, Table 3); SEC eluograms of the products: (1) PMMA homopolymer, RI detection; (2) final product, RI detection and (3) final product, UV detection.

3.3. Block copolymerization of MMA and t-BuA

This copolymerization was already briefly studied earlier [30]. Now, the MMA/*t*-BuA block copolymerization was performed in THF at −60 and −78 °C, respectively, and in toluene/THF mixture at −78 °C; for results, see Table 4. Run 1 in the table describes block copolymerization at −60 °C; a product with clearly bimodal MWD was formed, which is in perfect agreement with the results published in the recent paper [30].

Lowering the reaction temperature down to −78 °C leads to a reduced amount of the low-molecular-weight part in the final products of copolymerizations in THF (run 2) as well as in a toluene/THF mixture (run 3). Nevertheless, also at this temperature, the shoulders on the SEC eluograms

Table 4
Block copolymerization of MMA with *t*-BuA

Run	T (°C)	1st step[a]				2nd step				
		Time (min)	Conv. (%)	SEC		M_1:M_2	Time (min)	Conv. (%)	SEC	
				M_n	M_w/M_n				M_n[b]	M_w/M_n
1	−60	100	~100	10,400	1.17	1:1	120	83	21,500[c], 31,600[d]	1.30, 1.03
2	−78	180	95	8600	1.31	1:1	900	92	19,800[c], 26,100[d]	1.29, 1.04
3[e]	−78	180	~100	9600	1.22	1:1	900	91	24,600[c], 33,800[d]	1.27, 1.03

[a] MMA:MIB-Li:*t*-BuOLi mole ratio = 50:1:10; THF.

[b] Calculated as P*t*-BuA.

[c] Calculated from total eluogram, i.e. major peak plus low-molecular-weight peak.

[d] Calculated from major peak only.

[e] In toluene/THF mixture 50/50.

(Fig. 9) towards the low-molecular-weight region indicate an appreciable extent of termination of the living PMMA after addition of *t*-BuA, regardless of the reaction medium used. Thus, in all MMA/*t*-BuA block copolymerizations performed at both reaction temperatures, the high-molecular-weight peaks represent true poly(MMA-*b*-*t*-BuA) copolymers, having, if treated separately, symmetric and narrow MWDs. This can be seen from the M_n and M_w/M_n values of these peaks in Table 4 which were obtained using the Mark–Houwink–Sakurada constants for the P*t*-BuA/THF system [47]. On the other hand, the low-molecular-weight peaks of the eluograms belong likely to PMMA chains with a few *t*-BuA units, self-terminated by back-biting reaction. Although the ligated anionic homopolymerization of *t*-BuA exhibits, in comparison with other acrylates, generally a very low extent of self-termination by back-biting reaction [9,10], surprisingly, this is not true in MMA/acrylate block copolymerizations. As demonstrated above, the extent of self-termination of PMMA chains after addition of *t*-BuA is distinctly higher than in the block copolymerizations of MMA with the other acrylates. It can be speculated that the reasons for this behavior could consist in very different rates of propagation of *n*-alkyl acrylates and *t*-BuA. Preliminary kinetic measurements (not presented here) indicate that, for instance, EtHA polymerization, initiated with living PMMA (Table 1, run 1) reaches quantitative acrylate conversion in ca. 5 min, whereas *t*-BuA polymerization under the same conditions (Table 4, run 1) requires several hours for a high conversion to be reached. Moreover, an induction period was observed in the model study of *t*-BuA polymerization initiated with tBIB-Li at room temperature [48]. In contrast, BuA polymerization, initiated also with tBIB-Li in a toluene/THF mixture proceeds very rapidly even at low temperatures and in the presence of an excess of the alkoxide, so that the quantitative monomer conversion is reached in ca. 1.5 min [46,49].

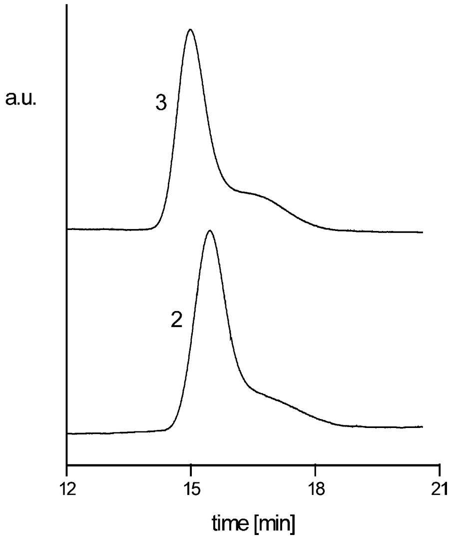


Fig. 9. SEC eluograms of the final products of MMA/*t*-BuA block copolymerization: the curve numbers correspond to the runs in Table 4.

4. Conclusion

Diblock copolymers of MMA with EtHA, BuA or EtA were successfully prepared by LAP initiated with the MIB-Li/*t*-BuOLi initiating system (1:10 mole ratio) a in toluene/THF mixture at −78 °C. At this temperature and in the presence on an excess of the alkoxide, the extent of self-termination is sufficiently low so that copolymers with fairly good molecular parameters are formed, containing a very low amount of PMMA from the first polymerization step. In particular, MMA/EtHA block copolymerization gives copolymers with clearly unimodal narrow MWD indicating thus a virtually negligible extent of spontaneous termination, particularly that proceeding just after the addition of acrylate. Moreover, MWD of the final product ($M_w/M_n = 1.12$) is narrower than that of the PMMA precursor ($M_w/M_n = 1.23$). In MMA/BuA copolymerization, the polydispersity index of the copolymer ($M_w/M_n = 1.26$) is almost the same as that of the corresponding PMMA

($M_w/M_n = 1.28$). However, MWD is somewhat non-symmetric towards the low-molecular-weight region, probably as a consequence of non-negligible extent of self-termination during the BuA polymerization. A more appreciable broadening of the MWD of final product can be observed in MMA/EtA polymerization performed under the same reaction conditions. Here, $M_w/M_n = 1.34$ for PMMA homopolymer and 1.36 for block copolymer and SEC eluogram of the final product is less symmetric than that of poly(MMA-*b*-BuA) copolymer. These observations are in agreement with increasing tendency of acrylic esters to side reactions, namely to self-termination by back-biting reaction, in the order EtHA < BuA < EtA. Somewhat surprisingly, the highest amount of low-molecular-weight self-terminated part can be observed in the final product of MMA/*t*-BuA block copolymerization even at −78 °C. The reasons for this rather unexpected behavior are not clear. It can be speculated that a less advantageous ratio of propagation and self-termination rate constants (k_p/k_t), in comparison with block copolymerizations of other acrylates, leads to a larger extent of self-termination by back-biting reaction in this case.

Acknowledgements

The authors thank Mr Štěpán Adamec for his skillful technical help. Financial support of the Academy of Sciences of the Czech Republic (project AVOZ 4050913) is greatly acknowledged.

References

[1] Hsieh HL, Quirk RP. Anionic polymerization. Principles and practice. New York, USA: Marcel Dekker; 1996.

[2] Wiles DM, Bywater S. J Phys Chem 1964;68:1983.

[3] Kawabata N, Tsuruta T. Makromol Chem 1965;86:231.

[4] Hatada K, Kitayama T, Fimikawa K, Ohta K, Yuki H. Polym Bull 1978;1:103.

[5] Webster OW, Hertler WR, Sogah DY, Farnham WB, Rajanbabu TV. J Am Chem Soc 1983;105:5706.

[6] Reetz MT, Knauf T, Minet U, Bingel C. Angew Chem 1988;100:1422.

[7] Aida T. Prog Polym Sci 1994;19:469.

[8] Yasuda H, Yamamoto H, Yokota K, Miyake S, Nakanuta A. J Am Chem Soc 1992;114:4908.

[9] Baskaran D. Prog Polym Sci 2003;28:521.

[10] Vlček P, Lochmann L. Prog Polym Sci 1999;24:793.

[11] Lochmann L, Kolařík J, Doskočilová D, Vozka S, Trekoval J. J Polym Sci, Polym Chem Ed 1979;17:1727.

[12] Vlček P, Lochmann L, Otoupalová J. Makromol Chem, Rapid Commun 1992;13:163.

[13] Fayt R, Forte R, Jacobs C, Jérôme R, Ouhadi T, Teyssié Ph. Macromolecules 1987;20:1442.

[14] Klein JW, Gnanou Y, Rempp P. Polym Bull 1990;24:39.

[15] Bayard P, Jérôme R, Teyssié Ph, Varshney SK, Wang JS. Polym Bull 1994;32:381.

[16] Nugay N, Nugay T, Jérôme R, Teyssié Ph. J Polym Sci, Part A: Polym Chem 1997;35:361.

[17] Baskaran D. Macromol Chem Phys 2000;201:890.

[18] Ballard DHG, Bowles RJ, Haddleton DM, Richards SN, Sellens R, Twose DL. Macromolecules 1992;25:5907.

[19] Haddleton DM, Muir AVG, O'Donnel JP, Richards SN, Twose DL. Macromol Symp 1995;91:93.

[20] Schlaad H, Schmitt B, Müller AHE, Jungling S, Weiss H. Macromolecules 1998;31:573.

[21] Schlaad H, Müller AHE. Macromolecules 1998;31:7127.

[22] Baskaran D, Sivaram S. Macromolecules 1997;30:1550.

[23] Zundel T, Teyssié Ph, Jérôme R. Macromolecules 1998;31:2433.

[24] Lochmann L, Pospíšil J, Vodňanský J, Lím D. Collect Czech Chem Commun 1965;30:2187.

[25] Kříž J, Dybal J, Janata M, Vlček P. Magn Res Chem 1994;32:8.

[26] Wang JS, Jérôme R, Warin R, Zhang H, Teyssié Ph. Macromolecules 1994;27:3376.

[27] Kříž J, Dybal J, Janata M, Vlček P. Macromol Chem Phys 1995;196:3117.

[28] Vlček P, Otoupalová J, Kříž J, Schmidt P. Macromol Symp 2000;161:113.

[29] Vlček P, Otoupalová J, Janata M, Polická P, Masař B, Toman L. Polymer 2002;43:7179.

[30] Vlček P, Otoupalová J, Janata M, Látalová P, Kurková D, Toman L, et al. Macromolecules 2004;37:344.

[31] Varshney SK, Jacobs C, Hautekeer JP, Bayard Ph, Jérôme R, Fayt R, et al. Macromolecules 1991;24:4997.

[32] Jacobs C, Varshney SK, Hautekeer JP, Fayt R, Jérôme R, Teyssié Ph. Macromolecules 1990;23:4024.

[33] Hosokawa Y, Kuroki M, Aida T, Inoue S. Macromolecules 1991;24:824.

[34] Ihara E, Morimoto M, Yasuda H. Macromolecules 1995;28:7886.

[35] Yasuda H, Ihara E, Nitto Y, Kakehi T, Morimoto M, Nodino M. In: Patil AO, Schulz DN, Novak BM, editors. Functional polymers. Modern synthetic methods and novel structures. ACS symposium series, vol. 704, 1998. p. 149.

[36] Wang JS, Jérôme R, Bayard P, Teyssié Ph. Macromolecules 1995;27:4908.

[37] Nugay N, Nugay T, Jérôme R, Teyssié Ph. J Polym Sci, Part A: Polym Chem 1997;35:1543.

[38] Vlček P, Otoupalová J, Sikora A, Kříž J. Macromolecules 1995;28:7262.

[39] Lochmann L, Lím D. J Organomet Chem 1973;9:50.

[40] Trekoval J, Lím D. J Polym Sci 1964;C4:333.

[41] Vlček P, Kříž J. J Polym Sci, Part A: Polym Chem 1992;30:1511.

[42] Brandrup J, Immergut EH, Grulke EA. Polymer handbook. New York: Wiley; 1999.

[43] Janata M, Lochmann L, Müller AHE. Makromol Chem 1993;194:625.

[44] Mrkvičková L, Daňhelka J, Vlček P. Polym Commun 1990;31:416.

[45] Vlček P, Otoupalová J, Jakeš J. Polym Prepr (Am Chem Soc, Div Polym Chem) 1997;38(1):491.

[46] Dvořánek L, Vlček P. Macromolecules 1994;27:4881.

[47] Mrkvičková L, Daňhelka J. J Appl Polym Sci 1990;41:1929.

[48] Janata M. PhD Thesis. Prague: Institute of Macromolecular Chemistry; 1989.

[49] Dvořánek L, Vlček P. Polym Bull 1993;31:393.

[50] Vlček P, Jakeš J, Otoupalová J. Collect Czech Chem Commun 1993;58:2565.

[51] Wang JS, Bayard Ph, Jèrôme R, Varshney SK, Teyssié Ph. Macromolecules 1994;27:4890.

[52] Zundel T, Teyssié Ph, Jèrôme R. Macromolecules 1998;31:5577.